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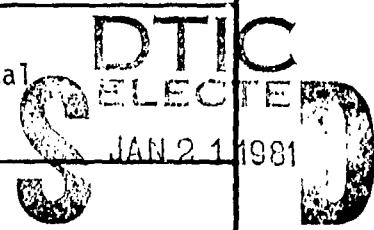
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TECHNICAL REPORT NO. 25

PHOTOCHEMISTRY OF METAL-METAL BONDED TRANSITION ELEMENT COMPLEXES

by

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Photochemistry of Metal-Metal Bonded Transition Element Complexes

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Transition metal complexes that have direct metal-metal bonds have been the objects of intense interest from the point of view of geometric and electronic structure, synthesis and catalysis (1, 2, 3, 4). Low-lying electronic excited states of metal-metal bonded complexes often involve significant changes in the electron density associated with the metal-metal bond, compared to the ground electronic state. Accordingly, study of the photochemistry of metal-metal bonded complexes not only provides potential new reaction chemistry but also provides insight into, and confirmation of, the electronic structure. This symposium volume affords us an opportunity to record the state of the field of metal-metal bond photochemistry. The aim of this article is to summarize recent research results from this laboratory and to place them in perspective in relation to results from other laboratories.

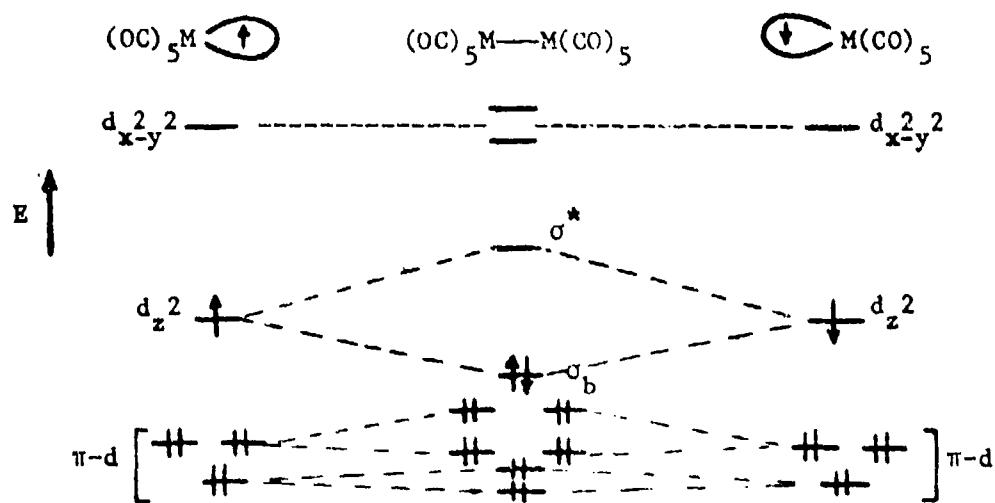
Complexes studied in this laboratory have included low-valent, organometallic clusters having two, three, or four metals. A priori the photoexcited complexes can be expected to undergo any reaction that is possible, but the rate constant for a given process will be different for each electronic state. Whether reaction occurs with measurable yield from a given excited state depends on the rate of the reaction relative to internal conversion of the excited state to a lower lying excited state. From an examination of products alone, therefore, it is not always possible to quantitatively assess the relative reactivity of the various electronic states. But when photochemical products differ from those obtained by thermal activation alone, profound effects from the redistribution of electron density can be inferred. In some cases the excited state may simply give the same product as from thermal activation of the ground state. However, when photoreaction occurs it should be realized that the conversion to product occurs within the lifetime of the excited state. Even the longest-lived excited metal complexes are of the order of  $10^{-3}$  s (5, 6) in lifetime and the longest-lived metal-metal bonded complex in 298 K fluid solution is of the order of  $\sim 10^{-6}$  s in lifetime (7). Thus, excited state reactions of any kind must

have large rate constants compared to those for the thermally inert ground state species. Measuring the rate constant for a given chemical reaction in two different electronic states is a procedure for directly assessing the relative chemical reactivity of the two states.

In the sections below we will describe in detail the known photochemistry of di-, tri-, and tetrานuclear metal clusters. Results will be discussed in simple electronic structural terms.

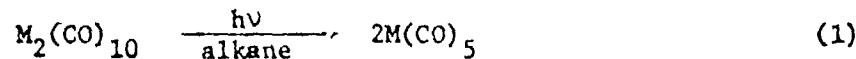
#### Photochemistry of Dinuclear Complexes

a. Complexes Having Single M-M Bonds and  $\pi$ -d  $\rightarrow$   $\sigma^*$  or  $\sigma_b$   $\rightarrow$   $\sigma^*$   
Lowest Excited States. It is apparent from the description of the electronic structure of  $Mn_2(CO)_{10}$ , (8, 9), Scheme I, that complexes having a single M-M bond could have low-lying excited states that should be more labile than the ground state with respect to either M-ligand dissociation or M-M bond cleavage. In particular,  $Mn_2(CO)_{10}$  and its third row analogue,  $Re_2(CO)_{10}$ , exhibit low-lying excited states arising from  $\pi$ -d  $\rightarrow$   $\sigma^*$  and  $\sigma_b$   $\rightarrow$   $\sigma^*$  transitions (8, 9, 10, 11). These high symmetry,

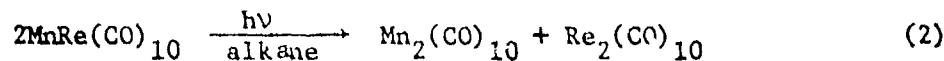


Scheme I. One-electron level diagram for  
 $Mn_2(CO)_{10}$ ,  $Re_2(CO)_{10}$ ,  $W_2(CO)_{10}^{2-}$ , etc.

"d<sup>7</sup> - d<sup>7</sup>", homodinuclear dimers were the first to be subjected to a detailed photochemical investigation (10, 11). Irradiation resulting in π-d → σ\* or σ<sub>b</sub> → σ\* transitions results in clean, quantum efficient, homolytic scission of the M-M bond to yield reactive, 17-valence electron radicals, equation (1) (10, 11).

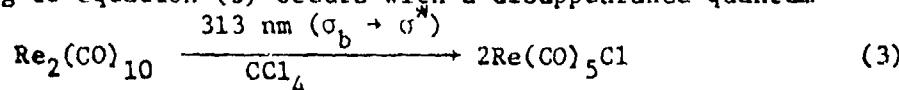


The generation of 17-valence electron radicals is consistent with flash irradiation of the heterodinuclear dimer MnRe(CO)<sub>10</sub> that yields radical coupling products according to equation (2)



(11, 12). Photogeneration of MnRe(CO)<sub>10</sub> from irradiation of both Mn<sub>2</sub>(CO)<sub>10</sub> and Re<sub>2</sub>(CO)<sub>10</sub> also occurs, and such cross-coupling has become a definitive test of whether homolytic metal-metal bond cleavage occurs. Kinetics of recovery of ground state Mn<sub>2</sub>(CO)<sub>10</sub> absorption after flash irradiations are consistent with formation of Mn(CO)<sub>5</sub> radicals from the excitation (13).

Irradiation of M<sub>2</sub>(CO)<sub>10</sub> in the presence of halogen donors provides chemical evidence consistent with the quantum efficient generation of 17-valence electron radicals (6). Chemistry according to equation (3) occurs with a disappearance quantum

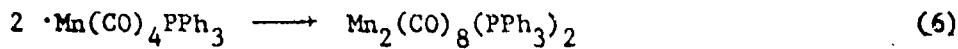
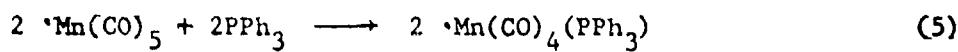


yield of 0.6 (10), showing that greater than half of the excited states yield the cleavage reaction. The efficiency of homolytic cleavage may be greater since cage escape of Re(CO)<sub>5</sub> radicals may be less than unity. There is a solvent viscosity effect on the disappearance quantum yield of M<sub>2</sub>(CO)<sub>10</sub> in the presence of I<sub>2</sub>, consistent with a solvent cage effect (11).

In polar solvents (pyridine, THF, alcohols, etc.) the photochemistry of simple M-M bonded systems seems to be different based on the products observed (14, 15). For example, irradiation of Mn<sub>2</sub>(CO)<sub>10</sub> can give Mn(CO)<sub>5</sub><sup>-</sup>. But this chemistry very likely originates from the 17-valence radical as the primary product. Disproportionation of the 17-valence electron species, perhaps after substitution at the radical stage, can account for the apparent heterolytic cleavage. If the excited state reaction is truly dissociative, as the evidence from cross-coupling in alkane suggests, there should be little or no influence from solvent.

Population of the σ\* orbital in M<sub>2</sub>(CO)<sub>10</sub> should stabilize the M-CO bond, (8, 9) and such is likely the case. However, prompt CO loss apparently does not compete with scission of the M-M bond. Irradiation of M<sub>2</sub>(CO)<sub>10</sub> in the presence of potential entering ligands such as PPh<sub>3</sub> does lead to substitution (5, 6, 11), but the principal primary photoproduct suggests a mechanism other than dissociative loss of CO to give M<sub>2</sub>(CO)<sub>9</sub>. For example,

irradiation of  $Mn_2(CO)_{10}$  in the presence of  $PPh_3$  leads to mainly  $Mn_2(CO)_8(PPh_3)_2$  rather than the expected  $Mn_2(CO)_9PPh_3$  (11). This led to the postulated mechanism represented by equations (4)-(6). The substitution lability of 17-valence electron radicals



has been elegantly elaborated by T. L. Brown and his co-workers (16, 17, 18, 19).

The population of the  $\sigma^*$  orbital in  $M_2(CO)_{10}$  obviously gives rise to considerable lability of the M-M bond. The ground state of these molecules is inert; the high quantum efficiency for photoreaction means that virtually every excited state produced yields radicals. The excited state cleavage rates can be concluded to be  $>10^{10} s^{-1}$ , since no emission has ever been detected from these species and the reactions cannot be quenched by energy transfer. The excited state cleavage rate of  $>10^{10} s^{-1}$  is many orders of magnitude larger than from the ground state and reflects the possible consequence of a one-electron excitation. The question of whether both depopulation of  $\sigma_b$  and population of  $\sigma^*$  are necessary is seemingly answered by noting that irradiation at the low energy tail of the  $\pi-d \rightarrow \sigma^*$  absorption gives a quantum yield nearly the same as that for  $\sigma_b \rightarrow \sigma^*$  excitation. However, the relative quantum yields do not reflect the relative excited state rate constants for reaction. It is only safe to conclude that either  $\pi-d \rightarrow \sigma^*$  or  $\sigma_b \rightarrow \sigma^*$  results in dramatic labilization compared to ground state reactivity and that the rate constant is large enough in each case to compete with internal conversion to an unreactive state. Another ambiguity is that the state achieved by a given wavelength may not be the state from which reaction occurs. The reactive states, for example, could be triplet states that only give rise to weak absorptions from the ground state.

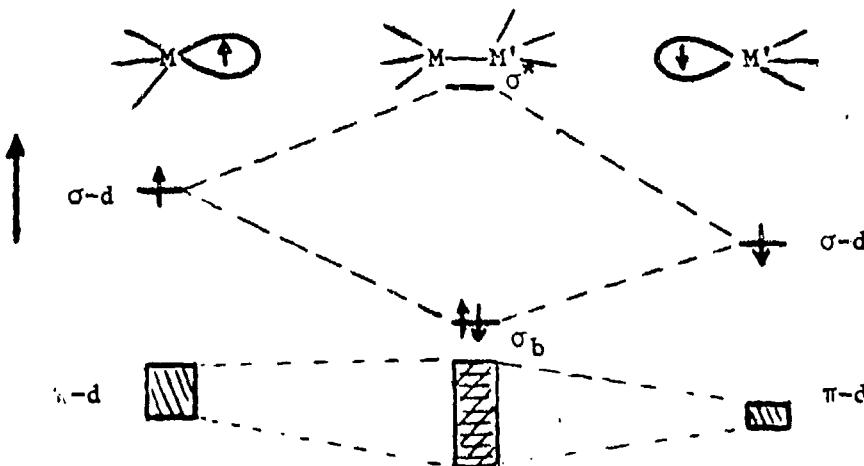
Electrochemistry and redox chemistry provide possible ways of assessing the consequence of one-electron depopulation or population of orbitals. The  $M_2(CO)_{10}$  species suffer rapid M-M cleavage upon reduction (population of  $\sigma^*$ ) or oxidation (depopulation of  $\sigma_b$ ) (20, 21). But cyclic voltammetry only reveals that the cleavage rate from the radical anion,  $M_2(CO)_{10}^-$ , or radical cation,  $M_2(CO)_{10}^+$ , is  $>\sim 10^3 s^{-1}$ . This is certainly consistent but direct measurements of the rate remain to be done.

Comparison of the photochemistry and the thermal reactivity of  $M_2(CO)_{10}$  is of interest. Considerable effort has been expended to show that thermolysis can lead to M-M bond cleavage. The activation energy from M-M dissociation has been examined and correlated with the position of the  $\sigma_b \rightarrow \sigma^*$  absorption band from

a number of derivatives of  $Mn_2(CO)_{10}$ . The question is: what is the relative importance of M-ligand cleavage vs., M-M cleavage in the ground state? A recent report bears on this question. Thermal reaction of  $MnRe(CO)_{10}$  with  $PPh_3$  was examined (22). The interesting finding is that the primary products do not include  $Mn_2(CO)_8(PPh_3)_2$  which would be expected if  $Mn(CO)_5$  were produced in the rate limiting step (see equations (4)-(6)). Thus, the ground state pathway for this complex appears to be mainly CO loss, not Mn-Re bond cleavage. The photoreactivity appears to be dominated by Mn-Re bond cleavage (11). A difference in M-ligand vs. M-M cleavage is seemingly established. The excited state results in a relatively low barrier to M-M cleavage compared to M-ligand cleavage. Since the excited state reaction is so clean and quantum efficient (*vide infra*) it is tempting to generalize the specificity found for excited state M-M' cleavage in  $MnRe(CO)_{10}$ . But this generalization would require that the ground state have a lower activation energy for M-ligand cleavage than for M-M cleavage. Such is apparently not the case for certain species such as  $(\eta-C_5H_5)_2Cr_2(CO)_6$  that likely exist in solution in equilibrium with the  $(\eta-C_5H_5)Cr(CO)_3$  radical (23). The species  $[(\eta^3\text{-allyl})Fe(CO)_3]_2$  also exists in the onomeric form in solution (24). Weak M-M single bonds do exist and the ground state M-M cleavage can clearly dominate the chemistry. Light may serve only to accelerate the observed rate.

There are now known a large number of other photosensitive dinuclear complexes that can be formulated as having a 2-electron sigma bond (25-29). Designation of the electronic configuration by the  $d^n$  configuration of the 17-valence electron fragment that would be obtained by homolytic cleavage allows a convenient cataloguing of the species studied so far. The transition metal-metal bonded complexes in the summary, Table I, have all been shown to undergo efficient M-M bond homolysis upon photo-excitation (11, 25-29). Examples of  $d^5-d^5$ ,  $d^7-d^7$ ,  $d^9-d^9$ ,  $d^5-d^7$ ,  $d^7-d^9$ , and  $d^5-d^9$  are all known. All of the complexes exhibit an optical absorption spectral feature in the near-uv or high energy visible that can be attributed to the  $\sigma_b + \sigma^*$  transition. Generally, a  $\pi-d + \sigma$  feature is also observable at lower energy than the  $\sigma_b + \sigma^*$ , and irradiation at this energy results in homolysis but with a somewhat lower quantum yield. None of the complexes listed are complicated by bridging ligands (see succeeding section) and none give significant yields for CO loss as the primary photoprocess.

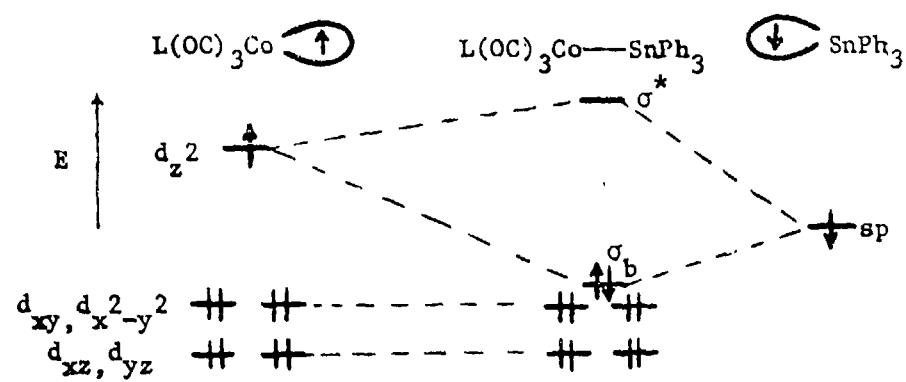
All of the M-M single bonded complexes can be formulated within the framework suggested by Scheme II. The 17-valence electron radicals studied all have about the same group electronegativity based on the ability to predict the position of the  $\sigma_b + \sigma^*$  absorption of heterodinuclear dimers, M-M' from the  $\sigma_b + \sigma^*$  energy in M-M and M'-M' (28). Significant ionic contribution to the M-M' bond will likely result in a situation where M-M' bond cleavage is heterolytic or where some other reaction, M-ligand cleavage for example, dominates the excited



Scheme II. General one-electron level diagram for  $M-M'$  single bonded complexes.

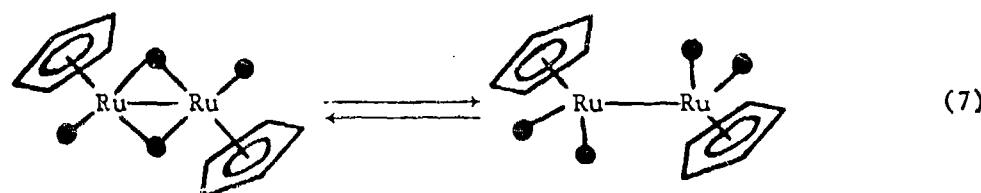
state processes. Irradiation of the  $(\eta\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{X}$  ( $\text{M} = \text{Mo}$ ,  $\text{W}$ ) (30),  $(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{X}$  (31), or  $\text{Re}(\text{CO})_5\text{X}$  (32) ( $\text{X} = \text{halide or pseudohalide}$ ) yields CO extrusion; in these cases the  $\sigma_b \rightarrow \sigma^*$  transition is very high in energy.

Complexes that exhibit a formal two-electron sigma bond between a transition metal and main group metal are of interest but have received relatively little study. Species such as  $(\text{CH}_3)_3\text{SnMn}(\text{CO})_5$  are thermally quite rugged but are photo-sensitive (33). Irradiation of  $(\eta\text{-C}_5\text{H}_5)\text{Mo}(\text{CO})_3\text{SnMe}_3$  in the presence of  $\text{P}(\text{OPh})_3$  yields CO substitution (34). The question of course is whether the primary photoreaction is loss of CO or homolysis of the Sn-M bond. The complexes  $\text{R}_3\text{SnCo}(\text{CO})_n\text{L}_{4-n}$  represent an interesting set of Sn-M bonded complexes, because the 17-valence electron Co-fragment is of  $d^9$  configuration and the complex has only one low-lying  $\sigma$  orbital. For example, Scheme III shows a simple, but very adequate, one-electron level diagram for  $\text{Ph}_3\text{SnCo}(\text{CO})_4\text{L}$ . Irradiation of this complex does not lead to efficient formation of  $\text{Co}_2(\text{CO})_6\text{L}_2$  that would be an expected cross-coupling product from photogenerated radicals. Rather, CO substitution occurs with a quantum yield of ~0.2 at 366 nm (35). The lowest excited state is very likely a  $\pi\text{-d} \rightarrow \sigma^*$  excitation and does not appear to result in sufficient Sn-M lability to compete with Co-Co cleavage within the excited state lifetime. The related system  $\text{R}_3\text{SiCo}(\text{CO})_4$  likewise only gives CO extrusion upon photoexcitation (36). In both of these systems the  $\sigma_b \rightarrow \sigma^*$  is likely much higher in energy than the  $\pi\text{-d} \rightarrow \sigma^*$  transitions. Even if the  $\sigma_b \rightarrow \sigma^*$  excitation is achieved it is not clear the Sn-M or Si-M bond cleavage can compete with M-CO cleavage rates in the excited state. It appears that bonds between group IV elements and transition metal carbonyls are not efficiently cleaved compared to the efficiency for M-CO cleavage.

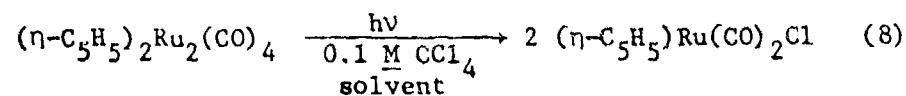


**Scheme III.** One-electron level diagram for a high symmetry  $d^9$ , 17-valence electron radical coupled to  $\text{Ph}_3\text{Sn}$ .

**b. Photochemistry of Bridged, M-M Single Bonded Complexes.** The unsupported M-M single bonds, Table I, give clean rupture of the M-M bond upon photoexcitation. Bridged M-M bonds represent a situation that could differ significantly since the bridging group could prevent the dissociation of the 17-valence electron fragments. The doubly CO-bridged  $\text{Co}_2(\text{CO})_8$ , and  $(\eta\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_4$  ( $\text{M} = \text{Fe}, \text{Ru}$ ) species have been examined. Of these, the most interesting is  $(\eta\text{-C}_5\text{H}_5)_2\text{Ru}_2(\text{CO})_4$  which exists as a non-bridged or bridged species, equation (7), in solution at 298 K. The



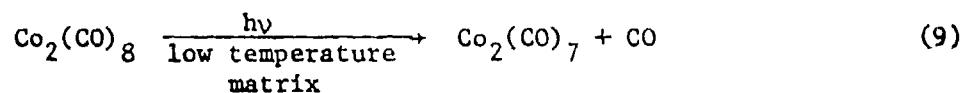
ratio of the two forms depends on the solvent with alkane solvents giving approximately a 1/1 ratio, while polar solvents such as  $\text{CH}_3\text{CN}$  give nearly 100% of the bridged form (37, 38). The 366 nm quantum yield for reaction according to equation (8) is



essentially the same in CH<sub>3</sub>CN and in isoctane where the fraction of incident light absorbed by the non-bridged form changes dramatically (38). The lack of a change in the quantum yield suggests that the bridged species is cleaved as efficiently as the non-bridged species by excitation corresponding to transitions that lead to population of the σ\* orbital.

The (η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>4</sub> is fully bridged in any solvent. Irradiation at 298 K in the presence of CCl<sub>4</sub> accelerates the thermal rate of formation of (η-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub>Cl (38, 39). Light-induced cross-coupling of (η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>4</sub> with the radical precursors M<sub>2</sub>(CO)<sub>10</sub>, (M = Mn, Re) (η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>M<sub>2</sub>(CO)<sub>6</sub> (M = Mo, W) is observed (28, 40), consistent with clean photogeneration of the (η-C<sub>5</sub>H<sub>5</sub>)Fe(CO)<sub>2</sub> radical. Irradiation of (η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>4</sub> at low temperature in solutions containing P(OR)<sub>3</sub> results in an intermediate hypothesized to be a CO-bridged species that has a ruptured Fe-Fe bond (41). This intermediate can be used to account for the reactions of photoexcited (η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>Fe<sub>2</sub>(CO)<sub>4</sub> without invoking the prompt photogeneration of free radicals. However, the radical cross-coupling is likely best explained by the ultimate generation of the free radicals but this may not be required if the lifetime of the CO-bridged species not containing the Fe-Fe bond is sufficiently long. In any event, population of states where the σ\* orbital is populated leads to a significantly weakened M-M interaction and net cleavage does occur. Prompt CO ejection does not seem to be an important process for either the Fe or Ru species.

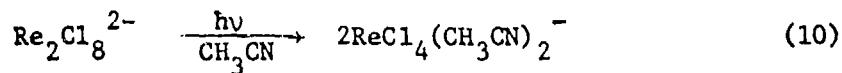
The Co<sub>2</sub>(CO)<sub>8</sub> also exists as bridged and non-bridged forms in solution (42). Irradiation of Co<sub>2</sub>(CO)<sub>8</sub> and (η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>M<sub>2</sub>(CO)<sub>6</sub> (M = Mo, W) leads to the expected radical coupling product (η-C<sub>5</sub>H<sub>5</sub>)M(CO)<sub>3</sub>Co(CO)<sub>4</sub> (28). But the quantum efficiency is not known. Irradiation of Co<sub>2</sub>(CO)<sub>8</sub> at low temperature has been shown to lead to loss of CO, equation (9), and the reaction is



wavelength dependent but quantum yields have not been reported (43). Reaction according to equation (9) leads to the suggestion that dissociative loss of CO can become the dominant photoreaction when the cage effect becomes severe enough to preclude separation of the 17-valence electron radicals. The importance of the bridging CO's in 298 K solutions is difficult to assess at this time. Some of the usual chemical probes are unsatisfactory here because the Co<sub>2</sub>(CO)<sub>8</sub> is labile thermally in the presence of potential entering ligands. The Co(CO)<sub>4</sub> radical does not seem to react rapidly enough with CCl<sub>4</sub> to provide a reasonable measure of the efficiency of the photogeneration of Co(CO)<sub>4</sub> (27, 28). The situation is further complicated by the fact that the Co(CO)<sub>4</sub>X (X = Cl, Br, I) species are thermally labile, even if formed.

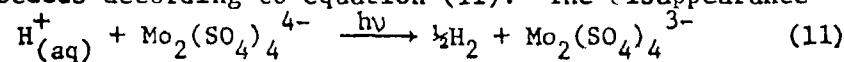
Intuitively, it would seem that bridging ligands would result in significantly lower quantum yields for M-M cleavage. Such is not found experimentally. If a retarding effect is to be quantitated it will likely come from a direct measurement of the excited state rate constants. Table II summarizes the key results to date.

c. Photochemistry of Dinuclear Complexes Having Multiple M-M Bonds. The cornerstone example of strong, multiple M-M bonds is the Re ≡ Re quadruple bonded  $\text{Re}_2\text{Cl}_8^{2-}$  (44). This substance was found to suffer Re ≡ Re bond cleavage from an upper excited state produced by optical excitation in  $\text{CH}_3\text{CN}$  solution, equation (10) (45). The lowest excited state, associated with the



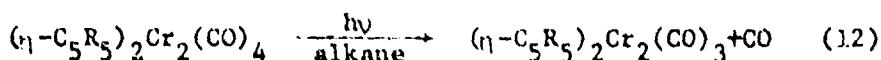
$\delta + \delta^*$  transition (46), is unreactive and apparently does not disrupt the bond enough to yield cleavage. Even the upper excited state suffers cleavage via attack of the  $\text{CH}_3\text{CN}$  as determined from flash photolysis studies (47). The photoinduced cleavage places an upper limit on the Re ≡ Re bond energy, but the energetics are obscured by the fact that reaction is not dissociative homolytic cleavage. The  $\text{Re}_2\text{Cl}_8^{2-}$  and  $\text{Re}_2\text{Br}_8^{2-}$  were found to be luminescent from the  $\delta + \delta$  excited state (48, 49). In the first report (48) describing the low temperature (1.3 K) emission of  $\text{Re}_2\text{X}_8^{2-}$  ( $X = \text{Cl}, \text{Br}$ ) and  $\text{Mo}_2\text{Cl}_8^{4-}$  the emission of ~100 ns lifetime was attributed to the triplet state, but subsequently (49) it was reported that the complexes  $\text{Re}_2\text{X}_8^{2-}$  and  $\text{Mo}_2\text{Cl}_4(\text{PR}_3)_4$  are emissive in fluid solution at 298 K with lifetimes in the 50-140 ns regime. The detailed study (49) led to the conclusion that the emission originates from a distorted singlet state. Related Mo ≡ Mo quadruple bonded complexes apparently do emit from a triplet state at low temperature (48) with a lifetime of ~2 ms for  $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$  at 1.3 K. The  $\text{Mo}_2\text{Cl}_4(\text{PR}_3)_4$  species have been found to undergo photooxidation in chlorocarbon solution (4, 50), but like the photochemistry for  $\text{Re}_2\text{X}_8^{2-}$  (45, 47), the reaction occurs from an upper excited state.

The Mo ≡ Mo quadruple bonded species  $\text{K}_4\text{Mo}_2(\text{SO}_4)_4$  has been irradiated in aqueous sulfuric acid solution (50). The photochemistry proceeds according to equation (11). The disappearance



quantum yield at 254 nm was found to be 0.17, but the reaction can also be effected with visible light. This system exemplifies the notion that if the lifetime of the excited state is not controlled by dissociative M-M bond cleavage, then bimolecular processes may be possible. The  $\text{Mo}_2(\text{SO}_4)_4^{4-}$  is another example of a multiple M-M bond that cannot be efficiently cleaved in a dissociative manner. Similarly, photoexcitation of  $\text{Mo}_2\text{X}_8^{4-}$  ( $X = \text{Cl}, \text{Br}$ ) in aqueous acid results in photooxidation. Clean formation of  $\text{Mo}_2\text{Cl}_8\text{H}^3$  can be observed. Again, rupture of the M ≡ M quadruple bond is not found (50).

Recent studies of the hydrocarbon soluble complexes  $(\eta\text{-C}_5\text{R}_5)_2\text{Cr}_2(\text{CO})_4$  ( $\text{R} = \text{H}, \text{Me}$ ) and  $(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)\text{Cr}_2(\text{CO})_4$ , that are formulated as having a  $\text{Cr} \equiv \text{Cr}$  triple bond, (51, 52) show that the dominant photoreaction is loss of CO according to equation (12) (53). The tricarbonyl species accounts for the



incorporation of  $^{13}\text{CO}$  upon irradiation of  $(\eta\text{-C}_5\text{R}_5)_2\text{Cr}_2(\text{CO})_4$  under a  $^{13}\text{CO}$  atmosphere. Irradiation of  $(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{R}_5)\text{Cr}_2(\text{CO})_4$  produces no detectable amount of  $(\eta\text{-C}_5\text{H}_5)_2\text{Cr}_2(\text{CO})_4$  or  $(\eta\text{-C}_5\text{Me}_5)_2\text{Cr}_2(\text{CO})_4$  and no measurable  $(\eta\text{-C}_5\text{H}_5)(\eta\text{-C}_5\text{Me}_5)\text{Cr}_2(\text{CO})_4$  is formed when a 1/1 mixture of the symmetrical species is irradiated. The negative results from the attempted cross-coupling experiments rule out an important role for the prompt generation of 15-valence electron fragments from photoexcitation of the  $\text{Cr} \equiv \text{Cr}$  triple bonded complexes. The quantum yield for loss of CO, equation (12), is wavelength dependent; irradiation at the lowest absorption (~600 nm) results in no reaction, but near-uv irradiation gives a quantum yield of  $>10^{-2}$  (53). The wavelength dependence is reminiscent of  $\text{Co}_2(\text{CO})_8$  in low temperature matrices where the potential fragments are tethered by the bridging groups and the cage effects of the matrix (43).

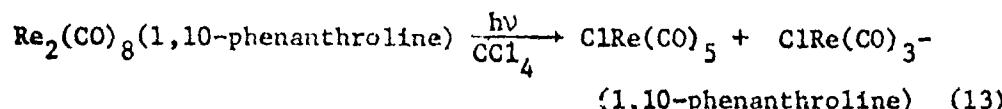
Irradiation of the  $(\eta\text{-C}_5\text{H}_5)_2\text{V}_2(\text{CO})_5$ , V=V double bonded species results in loss of CO, not V=V bond cleavage upon photoexcitation (54). The crucial result comes from an experiment where the  $(\eta\text{-C}_5\text{H}_5)_2\text{V}_2(\text{CO})_5$  is irradiated at  $-50^\circ\text{C}$  in the presence of  $\text{PEt}_2\text{Ph}$  in THF solution. The only product observed is  $(\eta\text{-C}_5\text{H}_5)_2\text{V}_2(\text{CO})_4\text{PEt}_2\text{Ph}$ .

From the studies of the quadruple, triple, and double bonded complexes examined thus far, it will prove difficult to photochemically cleave multiple metal-metal bonds in a dissociative fashion. Photochemical cleavage of multiple bonds is not taboo, since the light induced cleavage of  $\text{O}_2$  and  $\text{CO}_2$  is well known. But in metal complexes it appears that other processes such as solvent attack on the excited state, electron transfer, and ligand dissociation can lead to excited state deactivation before bond rupture can occur. As seen in the summary in Table III, dissociative cleavage of a multiple metal-metal bond remains to be accomplished. Also, upper excited state reaction is the rule in the multiple bonded systems.

d. Photochemistry of Dinuclear M-M Bonded Complexes Having Charge Transfer Lowest Excited States. Complexes such as  $\text{Re}(\text{CO})_5\text{Re}(\text{CO})_3(1,10\text{-phenanthroline})$  (55) and  $\text{Ph}_3\text{SnRe}(\text{CO})_3(1,10\text{-phenanthroline})$  (7, 56) and related complexes can be formulated as having a M-M or M'-M single bond. Table IV summarizes the known photoprocesses for such complexes. The lowest excited state in the complexes has been identified as arising from a  $(\text{M}-\text{M})_{\text{O}} + \pi$  phen charge transfer transition (7, 55, 56). Importantly, the orbital of termination of the

transition is not the  $\sigma^*$  orbital associated with the M-M or M-M' sigma bond. The orbital of termination is localized on the charge acceptor ligand and population of it is not expected to seriously disrupt the M-M or M-M' bonding. Consistent with this assertion is the fact that the complexes are reversibly reducible on the cyclic voltammetry time scale (56). However, the oxidation of the complexes is not reversible and cyclic voltammetry shows that M-M or M-M' cleavage occurs for the radical monocation at a rate of  $>10^5 \text{ s}^{-1}$  (56).

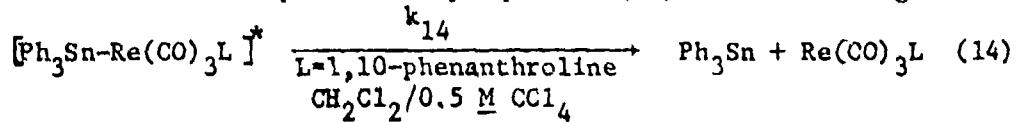
The lowest energy electronic transition of the  $\text{Re}_2(\text{CO})_8$ - (1,10-phenanthroline) and related complexes is expected to labilize the M-M bond in the sense that the  $\text{M}_2$ -core is "oxidized" by the intramolecular shift in electron density. Excitation has been shown to yield M-M bond cleavage; reaction according to equation (13) is representative (55). The quantum yield of ~0.2



was found to be independent of the excitation wavelength from 550 nm to 313 nm. This wavelength independent quantum yield is consistent with reaction that originates from the  $(\text{M}-\text{M})\sigma_b \rightarrow \pi^*$  phen CT state that is found to yield emission (but no photo-reaction) at low temperature. This result shows that depopulation of an M-M core bond level labilizes the M-M bond sufficiently to allow cleavage within the lifetime of the excited state. The 77 K emission lifetime was found to be extraordinarily long (~95  $\mu\text{sec}$ ), but emission was not detectable at all at 298 K where photoreaction occurs with a quantum yield of ~0.20. It is possible that emission is not observable at 298 K because M-M bond cleavage occurs too fast; this would indicate that the M-M dissociation rate in the excited state significantly exceeds  $10^5 \text{ s}^{-1}$ . Given that the ground state dissociation is slow ( $<10^{-6} \text{ s}^{-1}$ ) for these thermally inert (298 K) systems, even an excited state rate of  $10^5 \text{ s}^{-1}$  reflects an increase in dissociation rate of  $>10^{11}$  compared to the ground state. An excited state rate of  $>10^5 \text{ s}^{-1}$  is consistent with the lower limit of  $10^3 \text{ s}^{-1}$  cleavage rate of the radical monocation generated in electrochemical experiments.

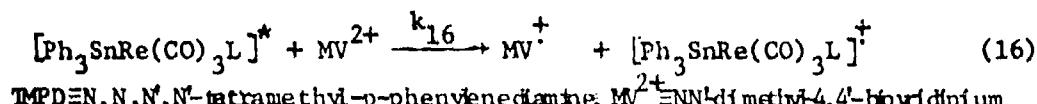
Study of  $\text{Ph}_3\text{SnRe}(\text{CO})_3$ (1,10-phenanthroline) resulted in the first direct determination of the rate constant for excited state cleavage of the M'-M bond (7, 56). The key is that this complex is emissive from the reactive state under the conditions where the cleavage reaction also occurs. Measurement of the emission lifetime ( $1.8 \times 10^{-6} \text{ s}$ ) and the photoreaction quantum yield (~0.23) give a rate constant of  $1.3 \times 10^5 \text{ s}^{-1}$  at 298 K for

the dissociation represented by equation (14). The wavelength

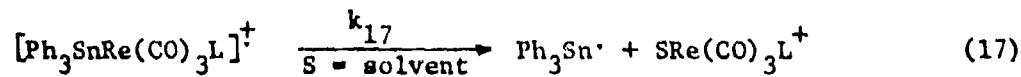


independence of photoreaction quantum yields (488-313 nm) and the ability to equally efficiently quench the lifetime, emission, and photoreaction with anthracene confirm that the emissive state is also the reactive state. The  $\sim 10^5 \text{ s}^{-1}$  excited state cleavage rate is consistent with the lower limit of  $10^3 \text{ s}^{-1}$  from cyclic voltammetry for cleavage of the radical monocation.

The relatively long lifetime of the lowest excited state of  $\text{Ph}_3\text{SnRe}(\text{CO})_3$  (1,10-phenanthroline) allows fast bimolecular processes to compete with the cleavage of the M-M bond (7). For example, anthracene, having a triplet energy of  $\sim 42 \text{ kcal/mol}$ , quenches the excited state ( $\sim 50 \text{ kcal/mol}$ ) at an essentially diffusion controlled rate by electronic energy transfer. The excited state can also be quenched by electron transfer, equations (15) and (16) (56). Both of these processes are



TPDEN, N,N,N',N'-tetramethyl-p-phenylenediamine;  $\text{MV}^{2+} = \text{NN'}\text{dimethyl-4,4'-bipyridinium}$  significantly downhill and the rate constants  $k_{15}$  and  $k_{16}$  are those expected for diffusion controlled reactions. The reduction to form  $[\text{Ph}_3\text{SnRe}(\text{CO})_3\text{L}]^-$  results in no net chemical change, since the back electron transfer is fast and the electron added to the Re complex in equation (15) is localized on L. The excited state oxidation though results in net chemistry, since chemistry according to equation (17) competes with the back electron



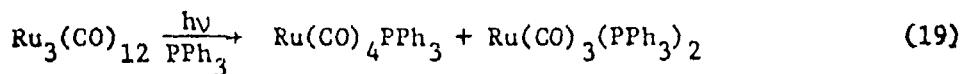
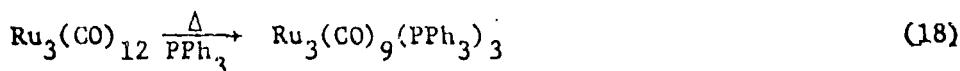
transfer. The unimolecular rate constant  $k_{17}$  is  $> 10^3 \text{ s}^{-1}$  from the electrochemistry and from the photochemistry (equation (14)) the value of  $k_{17}$  could be greater than  $10^5 \text{ s}^{-1}$ . The one-electron oxidants lead to production of 18-electron  $\text{SRe}(\text{CO})_3\text{L}^+$  products; this leads to the conclusion that the cleavage of  $[\text{Ph}_3\text{E}\text{Re}(\text{CO})_3\text{L}]^+$  yields  $\text{Ph}_3\text{E}^+$  and  $\text{Re}(\text{CO})_3\text{L}^+$ , not  $\text{Ph}_3\text{Sn}^+$  and  $\text{Re}(\text{CO})_3\text{L}$ .

The experiments with the various  $\text{M}-\text{Re}(\text{CO})_3\text{L}$  species establishes that population of the  $\sigma_b$  level is not required to achieve sufficient M-M bond lability to yield homolytic cleavage within the lifetime of the excited state. However, when the sigma bond order is reduced from one to approximately one-half by the depopulation of the  $\sigma_b$  level, the rate constant for M-M bond cleavage appears to be only  $\sim 10^5 \text{ s}^{-1}$ . By way of contrast, M-M bond cleavage seems to occur with a rate of  $> 10^{10} \text{ s}^{-1}$  for species

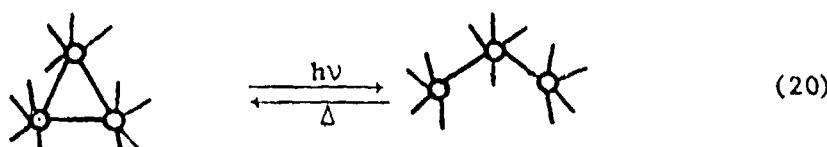
such as  $\text{Re}_2(\text{CO})_{10}$  where the sigma bond order is reduced from one to zero by the  $\sigma_b + \sigma^*$  excitation.

#### Photochemistry of Trinuclear Complexes

Table V summarizes the key photochemistry of trinuclear metal-metal bonded complexes. The first noteworthy photochemical study of trinuclear complexes concerns  $\text{Ru}_3(\text{CO})_{12}$ . This species was found to undergo declusterification to mononuclear fragments when irradiated in the presence of entering ligands such as CO,  $\text{PPh}_3$ , or ethylene. The intriguing finding is that thermal reaction of  $\text{Ru}_3(\text{CO})_{12}$  with  $\text{PPh}_3$  results in the substitution product indicated in equation (18) whereas irradiation yields the mono-nuclear species given by equation (19) (57). These results



suggest that Ru-Ru bond cleavage occurs in the excited state whereas Ru-CO dissociation occurs in the ground state. An electronic structural study shows that the orbital of termination for the lowest energy excited states of  $\text{Ru}_3(\text{CO})_{12}$  is  $\sigma^*$  with respect to the  $\text{Ru}_3$ -core (58). The disappearance quantum yields for  $\text{Ru}_3(\text{CO})_{12}$ ,  $\text{Fe}_3(\text{CO})_{12}$  and  $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$  are all in the range of  $10^{-2}$  for entering groups such as CO or  $\text{PPh}_3$  and are independent of entering group concentration (59, 60). The electronic structure is consistent with primary photoreaction as represented by equation (20), and the overall low quantum yields are consistent

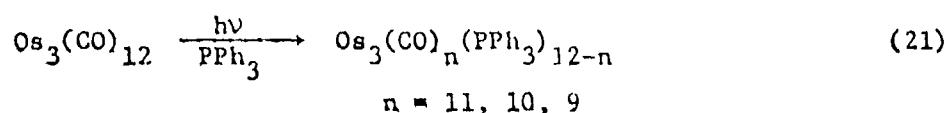


with efficient closure to regenerate the metal-metal bond.

Irradiation of  $\text{Ru}_3(\text{CO})_{12}$  (57, 60),  $\text{Fe}_3(\text{CO})_{12}$  (60), or  $\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$  (59) under CO cleanly leads to mononuclear complexes. This fact seems to rule out dissociative loss of CO as the dominant reaction from the excited state. If loss of CO were the dominant process, the presence of CO would simply retard the decomposition of the cluster. The lack of an effect from high concentrations of entering group (1-pentene or  $\text{PPh}_3$ ) on the quantum yield for photodeclusterification of  $\text{Fe}_3(\text{CO})_{12}$  or  $\text{Ru}_3(\text{CO})_{12}$  (60) is consistent with this conclusion.

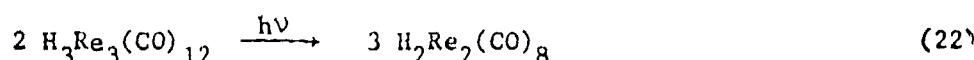
The lowest excited states of triangular trinuclear complexes, like dinuclear complexes, can also be labile with respect to loss

of CO as well as metal-metal bond cleavage. Irradiation of  $\text{Os}_3(\text{CO})_{12}$  under conditions where  $\text{Ru}_3(\text{CO})_{12}$  is declusterified leads to substitution of CO, equation (21) (60, 61). This



change in photoreactivity may be due to the fact that the lowest excited state is  $\sigma \rightarrow \sigma^*$  in the  $\text{Ru}_3(\text{CO})_{12}$  case whereas it is  $\sigma^* \rightarrow \sigma^*$  in the case of  $\text{Os}_3(\text{CO})_{12}$ . An alternative explanation may be simply that the stronger Os-Os bonds have lower dissociation rates while Os-CO and Ru-CO cleavage rates are similar. In any event, there is a striking difference in the qualitative features of  $M_3(\text{CO})_{12}$  ( $M = \text{Fe}, \text{Ru}$ ) vs.  $\text{Os}_3(\text{CO})_{12}$ . Absolute photoreaction quantum yields for any photoreaction are small, but it does appear that M-M bond cleavage dominates for  $M = \text{Ru}$  or  $\text{Fe}$  while M-CO cleavage dominates for  $M = \text{Os}$ .

The clean photodeclusterification represented by equation (22)



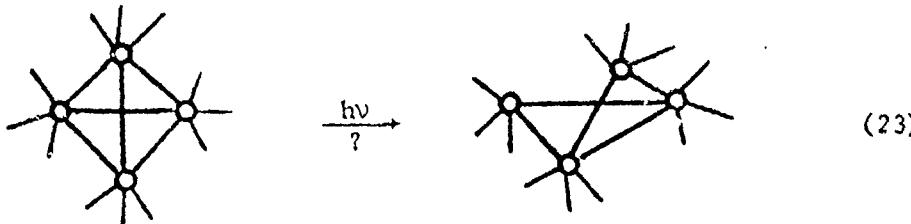
is a case where photoexcitation leading to either Re-Re cleavage or dissociative loss of CO could allow rationalization of the observed chemistry (62). The observed quantum yield of ~0.1 is the highest observed for a triangular metal-metal bonded system. This high quantum yield and the fact that the Re-Re bonds are bridged by H atoms suggest that the dissociative loss of CO is the likely result of photoexcitation in this case.

Photolysis of the complex  $\text{RCCo}_3(\text{CO})_9$  ( $\text{R} = \text{H}, \text{CH}_3$ ) under an  $\text{H}_2$  atmosphere has been reported to yield declusterification with low quantum efficiency (63). As in the case above it is not clear whether reaction begins with M-M or M-CO bond cleavage; the excited state should be more labile than the ground state with respect to either process.

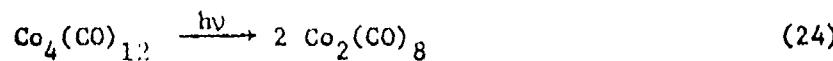
In contrast to the generally low quantum yields for the triangular- $M_3$  systems,  $\text{Os}_3(\text{CO})_{12}\text{Cl}_2$ , that has only two Os-Os bonds, undergoes photoinduced M-M bond cleavage with a high quantum yield (61). This result lends support to the assertion that the tethered diradical center, equation (20), may be important in giving net quantum yields that are low compared to species such as  $\text{Mn}_2(\text{CO})_{10}$ . A possible contribution to low quantum yields for the triangular- $M_3$  core systems is the fact that the one-electron excitations promoted by optical absorption are not simply localized labilization of two of the three bonds.

#### Photochemistry of Tetranuclear Complexes

Complexes having the tetrahedrane- $M_4$  core have six direct M-M bonds and it is not likely that one-electron excitation will result in enough bonding disruption to extrude mononuclear fragments. If an M-M bond does cleave, equation (23), cleavage of



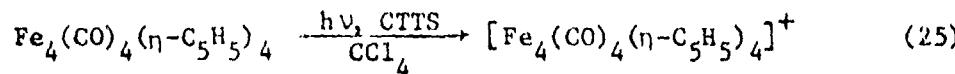
two other M-M bonds would be required in order to generate the mononuclear fragment. Cleavage in the sense suggested by equation (23) can seemingly occur, though, since photoreaction according to equation (24) has been observed (63). If



dissociative loss of CO occurs the presence of added CO would seemingly only lead to back reaction with no net chemical change. Likewise,  $\text{HFeCo}(\text{CO})_{12}$  yields  $\text{Co}_2(\text{CO})_8$  when irradiated under CO (63). The quantum yields for these reactions are low and it is not clear where the inefficiency lies: is the M-M bond cleavage (equation (23)) a low quantum yield process or is the reformation of the M-M so fast that it is inefficiently trapped by CO?

Irradiation of  $\text{Ir}_4(\text{CO})_{12}$  in the presence of  $(\text{MeCO}_2)_2\text{C}_2$  results in the retention of an  $\text{Ir}_4$  complex but the  $\text{Ir}_4$ -core in the  $\text{Ir}_4(\text{CO})_8[(\text{MeCO}_2)_2\text{C}_2]_4$  product is a rectangle. Such a product could arise from either CO loss or from trapping of a photogenerated diradical. As in the trinuclear  $\text{M}_3(\text{CO})_{12}$  complexes, the result for the  $\text{Ir}_4$  species ( $\text{Ir}_4$  retention) compared to the  $\text{Co}_4$  species (fragmentation (63)) may signal a trend in M-M bond retention for the third row systems where M-M bonds are expected to be stronger.

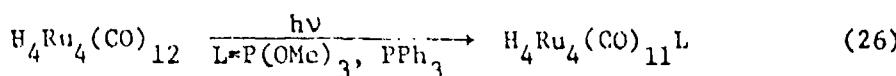
Not surprisingly, the tetranuclear  $\text{Fe}_4(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_4$ , that has a tetrahedrane- $\text{Fe}_4$  core with the CO's triply face bridging, is photoinert in solution with respect to Fe-Fe or Fe-CO bond rupture (65). In the presence of halocarbons such as  $\text{CCl}_4$  there is a clean photooxidation reaction, equation (25), resulting from



irradiation corresponding to absorption due to a charge transfer to solvent transition. Ferrocene exhibits a similar photo-reactivity (66); to extend the comparison it is noteworthy that the potential for ferrirenium/ferrocene and  $[\text{Fe}_4(\text{CO})_4(\eta\text{-C}_5\text{H}_5)]^+/0$  is nearly the same (67), the CTTS is at about the same energy and intensity for a given halocarbon, and the quantum yields for photooxidation (after correction for intramolecular absorption) are quite similar (68). The resilience of the  $\text{Fe}_4(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_4$  with respect to light induced bond cleavage reactions allows the

observation of the photooxidation process. A similar situation appears to exist for the quadruple bonded  $\text{Mo}_2(\text{SO}_4)_4^{2-}$  and  $\text{Mo}_2\text{Cl}_4(\text{PR}_3)_4$  described above (50).

Quantum inefficient ligand dissociation does appear to be the primary chemical result from photoexcitation of  $\text{H}_4\text{Ru}_4(\text{CO})_{12}$  (68). Irradiation at 436 or 366 nm in the presence of an entering ligand proceeds according to equation (26). The



reaction has the same quantum efficiency ( $5 \pm 1 \times 10^{-3}$ ) for  $\text{L} = \text{P}(\text{OMe})_3$  or  $\text{PPh}_3$  and for a variation in concentration of  $\text{L}$  from 0.01 to 0.1 M. These observations support the prompt generation of  $\text{H}_4\text{Ru}_4(\text{CO})_{11}$  from photoexcitation. The complex undergoes substitution thermally but photoexcitation accelerates the rate dramatically. Photoexcitation of  $\text{H}_4\text{Os}_4(\text{CO})_{12}$  does give chemistry and photoreaction may begin with dissociative loss of CO subsequent to photoexcitation (69).

Irradiation of  $\text{H}_4\text{Re}_4(\text{CO})_{12}$  does not result in any significant photoreaction (70). The lack of any Re-Re bond cleavage may be associated with the fact that the Re-Re bonds have multiple bond character (71). The  $\text{H}_4\text{Re}_4(\text{CO})_{12}$  exhibits emission from the lowest excited state. This finding prompted a comparison of the excited state decay of the  $\text{D}_4\text{Re}_4(\text{CO})_{12}$ . Generally, the highest energy vibrational modes are important in non-radiative decay (72), and for metal complexes the highest energy M-L vibrations may be most important. The hydrogen atoms in  $\text{H}_4\text{Re}_4(\text{CO})_{12}$  are believed to be triply face bridging (71) with a Re- $\text{H}$  stretching frequency of  $\sim 1023 \text{ cm}^{-1}$  (73). The  $\text{H}_4\text{Re}_4(\text{CO})_{12}$  complex emits in hydrocarbon solution or as the pure solid at 298 or 77 K. The emission ( $\sim 14,300 \text{ cm}^{-1}$ ) onset overlaps the absorption and thus a large distortion of the complex upon excitation does not appear to occur. The emitter can be quenched by the triplet quencher anthracene, having a triplet energy of  $\sim 42 \text{ kcal/mol}$  (74). The lifetime is in the range  $0.1 - 16 \mu\text{sec}$  depending on conditions and is of the order of 20-30% longer for the  $^2\text{H}$  substituted complex. Likewise the emission quantum yields for the  $\text{D}_4\text{Re}_4(\text{CO})_{12}$  are 20-30% longer than for the  $^4\text{H}$  species. Thus, replacing  $^4\text{H}$  by  $^2\text{H}$  in  $\text{H}_4\text{Re}_4(\text{CO})_{12}$  has the expected effect of reducing the rate of non-radiative decay. But the effect does not lead to a situation where the excited decay is dominated by the radiative decay rate.

The studies of the tetrahedrane- $\text{M}_4$  clusters, Table VI, show quite generally that the importance of dissociative processes within the excited state lifetime is low. Clean, but low quantum yield, photoreactions are detectable in some cases. The resistance of the complexes to declusterification may be exploited to study and utilize bimolecular processes, and in the case of the  $\text{H}_4\text{Re}_4(\text{CO})_{12}$  the reactions and non-chemical, non-radiative decay are sufficiently low that the excited state lifetime allows

radiative decay to be observed. Such long-lived excited states may allow the development of a bimolecular excited state chemistry of such species.

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Table I. Photochemistry of Dinuclear, M-M or M-M' Species Having a Two-Electron Sigma Bond.

Complex ( $d^n - d^n$ )	Primary Photoreaction (Ref.)	Comment
( $\eta\text{-C}_5\text{H}_5$ ) <sub>2</sub> M <sub>2</sub> (CO) <sub>6</sub> (M=Mo, W) ( $d^5-d^5$ )	M-M Bond Cleavage (25) (from cross-coupling and trapping reactions)	Population of $\sigma_b \rightarrow \sigma^*$ gives higher quantum yield than $\pi\text{-d} \rightarrow \sigma^*$ .
M <sub>2</sub> (CO) <sub>10</sub> (M=Mn, Re) ( $d^7-d^7$ ) MnRe(CO) <sub>10</sub> ( $d^7-d^7$ )	M-M or Re-Mn Cleavage (11) (from cross-coupling and trapping reactions)	Electronic structure well-established (8,9).
Co <sub>2</sub> (CO) <sub>6</sub> L <sub>2</sub> (L=P( $\eta\text{-Bu}$ ) <sub>3</sub> , P(OPh) <sub>3</sub> ( $d^9-d^9$ )	Co-Co Bond Cleavage (29) (from cross-coupling reactions)	Halogen atom abstraction products not stable at 298 K.
( $\eta\text{-C}_5\text{H}_5$ )Fe(CO) <sub>2</sub> Mn(CO) <sub>5</sub> ( $d^7-d^7$ )	Fe-Mn Bond Cleavage (40) (from cross-coupling reactions)	Heterodinuclear but same dn configuration at each center.
( $\eta\text{-C}_5\text{H}_5$ )Fe(CO) <sub>2</sub> M(CO) <sub>3</sub> ( $\eta\text{-C}_5\text{H}_5$ ) ( $d^7-d^5$ ) (M = Mo, W)	Fe-M Bond Cleavage (27,28,40) (from cross-coupling and halogen atom abstraction reactions)	
( $\eta\text{-C}_5\text{H}_5$ )Fe(CO) <sub>2</sub> Co(CO) <sub>3</sub> (P(CPh) <sub>3</sub> ) ( $d^7-d^9$ )	Fe-Co Bond Cleavage (29) (from cross-coupling reaction)	
( $\eta\text{-C}_5\text{H}_5$ )M(CO) <sub>3</sub> M'(CO) <sub>5</sub> ( $d^5-d^7$ ) (M=Mo, W; M'=Mn, Re)	M-M' Bond Cleavage (26) (from cross-coupling and halogen atom reactions)	Significantly lower quantum yield for $\pi\text{-d} \rightarrow \sigma^*$ vs. $\sigma_b \rightarrow \sigma^*$ .

Table I. (continued)

<u>Complex (<math>d^n - d^9</math>)</u>	<u>Primary Photoreaction (Ref.)</u>	<u>Comment</u>
$(\eta\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{CO}(\text{CO})_4$ ( $d^5-d^9$ )	M-Co Bond Cleavage (27, 28, 40) (from cross-coupling and halogen atom reactions)	
$(\eta\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3\text{SnMe}_3$ ( $d^5$ -main group)	Loss of CO (34) (from photosubstitution)	Loss of CO or Mn-Sn cleavage would rationalize results.
$\text{Mn}(\text{CO})_5\text{SnMe}_3$ ( $d^7$ -main group)	Not well-established (33)	
$\text{Co}(\text{CO})_3(\text{P}(\text{OPh})_3)\text{SnPh}_3$ ( $d^9$ -main group)	Loss of CO (35) (from photosubstitution)	

**Table II.** Photochemistry of Bridged Dinuclear Metal-Metal Bonded Complexes.

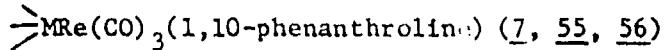
Complex	Photoreaction (Ref.)	Comment
$(\eta\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$	$(\eta\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4 \xrightarrow[\text{CCl}_4]{\text{h}\nu} 2(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2\text{Cl}$ (38,39)	Quantum yield reasonable but thermal reaction is detectable suggesting relatively small degree of labilization upon photoexcitation.
	$\xrightarrow[\text{hydrocarbon}]{\text{h}\nu} 2(\eta\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})_2^-$	Implies formation of free radicals.
	$\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3$ (28)	
	$(\eta\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4 + \text{P}(\text{OR})_3 \xrightarrow{\text{h}\nu}$	CO-bridged, Fe-Fe cleaved intermediate observed at low temperature (40).
	$(\eta\text{-C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_3\text{P}(\text{OR})_3$ (38,40)	
	$(\eta\text{-C}_5\text{H}_5)_2\text{Ru}_2(\text{CO})_4 \xrightarrow[\text{CCl}_4]{\text{h}\nu} 2(\eta\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{Cl}$ (38)	Quantum yield independent of whether 1/1 bridged/non-bridged or 100% bridged.
$(\eta\text{-C}_5\text{H}_5)_2\text{Ru}_2(\text{CO})_4$	$\text{Co}_2(\text{CO})_8 \xrightarrow[\text{low temp. matrix}]{\text{h}\nu} \text{Co}_2(\text{CO})_7 + \text{CO}$ (43)	Low temperature form is fully bridged; room temperature form is 1/1 in hydrocarbon solution.

Table II. (continued)

Complex	Photoreaction (Ref.)	Comment
$\text{Cc}_2(\text{CO})_8 + (\eta\text{-C}_5\text{H}_5)_2\text{M}_2(\text{CO})_6$	$\xrightarrow[\text{hydrocarbon}]{\text{hv}}$ $2(\eta\text{-C}_5\text{H}_5)\text{M}(\text{CO})_3\text{Co}(\text{CO})_4$ (27, 28)	

Table III. Photochemistry of Dinuclear M-M Multiple-Bonded Complexes.

Complex	M-M Bond Order	Primary Photoreaction (Ref.)
$\text{Re}_2\text{Cl}_8^{2-}$	4	Solvent attack of excited state leads to Re-Re Cleavage (45, 47)
$\text{Mo}_2\text{Cl}_4(\text{P}(\text{n-Bu})_3)_4$	4	Emits at 298 K or lower (49); Photooxidized in chlorocarbons (4, 50)
$\text{Mo}_2\text{X}_8^{4-}$	4	Emits at 1.3 K; photooxidized in $\text{H}_2\text{O}$ to give $\text{Mo}_2\text{X}_8^{\text{H}_5-}$ (48, 50)
$(\eta\text{-C}_5\text{R}_5)_2\text{Cr}_2(\text{CO})_4$ (R = Ne, H)	3	Dissociative loss of CO from upper excited states (53)
$(\eta\text{-C}_5\text{H}_5)_2\text{V}_2(\text{CO})_5$	2	Loss of CO (54)

Table IV. Primary Excited State Processes of

Complex	Photo process
$\text{Re}(\text{CO})_5\text{Re}(\text{CO})_3(1,10\text{-phenanthroline})$	Emission at 77 K Re-Re Bond Dissociation at 298 K
$\text{Ph}_3\text{ERe}(\text{CO})_3(1,10\text{-phenanthroline})$ (E = Sn, Ge)	Emission at 298 or 77 K E-Re Bond Dissociation Electronic Energy Transfer Electron Transfer

Table V. Photochemistry of Trinuclear M-M Bonded Complexes.

Complex	Primary Photoreaction (Ref.)
$\text{M}_3(\text{CO})_{12}$ (M = Fe, Ru)	M-M Cleavage is likely dominant (57, 59, 60) (low overall quantum yield).
$\text{Ru}_3(\text{CO})_9(\text{PPh}_3)_3$	Ru-Ru Bond Cleavage (59) (low overall quantum yield).
$\text{Os}_3(\text{CO})_{12}$	Dissociative loss of CO (60, 61) (low quantum yield),
$\text{Os}_3(\text{CO})_{12}\text{Cl}_2$	Os-Os Bond Cleavage; Linear Structure; High Quantum Yields (61)
$\text{H}_3\text{M}_3(\text{CO})_{12}$ (M = Mn, Re)	CO loss or M-M Bond Cleavage (62)
$\text{RCCo}_3(\text{CO})_9$ (R = $\text{CH}_3$ , H)	CO loss Co-Co Bond Cleavage (63)

Table VI. Photochemistry of Tetranuclear Complexes.

Complex	Photoprocess (Ref.)
$\text{Co}_4(\text{CO})_{12}$	Likely Co-Co Bond Cleavage; $\text{Co}_2(\text{CO})_8$ formed under CO (63)
$\text{HFeCo}_2(\text{CO})_{12}$	Primary process likely M-M Bond Cleavage (63)
$\text{Fe}_4(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_4$	Inert in Hydrocarbon; Photooxidation via CTTS in Halocarbon (65)
$\text{Ir}_4(\text{CO})_{12}$	Derivative with $\text{Ir}_4$ unit retained can be formed (64)
$\text{H}_4\text{Ru}_4(\text{CO})_{12}$	Loss of CO; Low Quantum yield (68)
$\text{H}_4\text{Os}_4(\text{CO})_{12}$	Loss of CO (69)
$\text{H}_4\text{Re}_4(\text{CO})_{12}$	Photoinert; Emits at 298 or 77 K (70)

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